

**INTERNET COOPERATION TREATY**  
**PCT**  
**INTERNATIONAL PRELIMINARY EXAMINATION REPORT**  
(PCT Article 36 and Rule 70)

REC'D 10 AUG 2004

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Applicant's or agent's file reference 482169 TVG	<b>FOR FURTHER ACTION</b>	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416).
International Application No. <b>PCT/NZ2003/000128</b>	International Filing Date (day/month/year) 24 June 2003	Priority Date (day/month/year) 24 June 2002
International Patent Classification (IPC) or national classification and IPC <b>Int. Cl. <sup>7</sup> A62D 3/00; C02F 1/72, 1/74, 1/78, 1/04; C07B 33/00</b>		
Applicant <b>VICTORIA LINK LIMITED et al</b>		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 3 sheets, including this cover sheet.

☒ This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 14 sheet(s).

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☐ Certain observations on the international application

Date of submission of the demand 23 January 2004	Date of completion of the report 3 August 2004
Name and mailing address of the IPEA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaaustralia.gov.au Facsimile No. (02) 6285 3929	Authorized Officer  <b>GAYE HOROBIN</b> Telephone No. (02) 6283 2069

**I. Basis of the report****1. With regard to the elements of the international application:\***

- ☐ the international application as originally filed.
- ☒ the description, pages 1,2,8,9,12-26, as originally filed,  
pages , filed with the demand,  
pages 3-7, 10, 11, 27, received on 26 July 2004 with the letter of 26 July 2004
- ☒ the claims, pages , as originally filed,  
pages , as amended (together with any statement) under Article 19,  
pages , filed with the demand,  
pages 28-32, received on 26 July 2004 with the letter of 26 July 2004
- ☒ the drawings, pages , as originally filed,  
pages , filed with the demand,  
pages , received on with the letter of
- ☐ the sequence listing part of the description:  
pages , as originally filed  
pages , filed with the demand  
pages , received on with the letter of

**2. With regard to the language, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.**

These elements were available or furnished to this Authority in the following language which is:

- ☐ the language of a translation furnished for the purposes of international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of the translation furnished for the purposes of international preliminary examination (under Rules 55.2 and/or 55.3).

**3. With regard to any nucleotide and/or amino acid sequence disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:**

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

**4. ☐ The amendments have resulted in the cancellation of:**

- ☐ the description, pages
- ☐ the claims, Nos.
- ☐ the drawings, sheets/fig.

**5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).\*\***

\* Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17).

\*\* Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report

**V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement****1. Statement**

Novelty (N)	Claims 1-39	YES
	Claims	NO
Inventive step (IS)	Claims 1-39	YES
	Claims	NO
Industrial applicability (IA)	Claims 1-39	YES
	Claims	NO

**2. Citations and explanations (Rule 70.7)****NOVELTY(N), INVENTIVE STEP(IS)**

No citation or obvious combination of citations discloses all of the features of the claimed invention. In particular the citations do not disclose the catalytic wet oxidation of a waste stream wherein the oxidation products are removed in the vapour phase and the liquid phase is retained in the reactor. In the prior art the liquid phase is discharged from the reactor either for disposal or further processing.

These disadvantages have hindered the development of wet oxidation as a method for treating waste. Accordingly, it is an object of the present invention to provide a wet oxidation process which goes some way to overcoming these limitations, or at least provides the public with a useful choice.

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## SUMMARY OF INVENTION

In a first aspect, the present invention provides a process for wet oxidation of a feedstock comprising at least one non-volatile oxidisable material, which process includes at least  
10 the steps of:

- (a) continuously introducing the feedstock into a reactor;
- (b) contacting the feedstock at temperature and pressure with an oxidant in the presence of a catalyst to produce a vapour phase comprising at least some oxidation products and a liquid phase; and
- 15 (c) continuously removing at least some of the vapour phase comprising at least some oxidation products from the reactor while retaining the liquid phase in the reactor.

The non-volatile oxidisable material may be a single substance or a mixture of substances, and may be a waste product such as industrial waste, consumer waste or a  
20 component thereof, all of which are well known in the art.

Generally the oxidisable material comprises an organic substance.

Preferably, the oxidisable material comprises one or more components selected from the  
25 group consisting of: lipids; proteins; carbohydrates (for example starch or cellulose); mineral oils; vegetable oils; waxes; and hydrocarbons.

Optionally, the oxidisable material includes one or more oxidisable inorganic compounds.

30 Oxidants which may be used in a process of the invention include, but are not limited to air, oxygen, ozone, peroxide, and mixtures thereof. Preferably, the oxidant is air, oxygen or peroxide.

The temperature at which the process is operated is generally between about 100°C and about 350°C and the pressure between 0.7 and 17.2 MPa.

5 Preferably, the temperature at which the process is operated is between about 190°C and about 300°C, more preferably between about 190°C and about 280°C. In two particularly preferred embodiments, the temperature is between about 190°C and about 210°C or between about 220°C and about 240°C.

10 Preferably, the pressure at which the process is operated is between about 1.4 MPa and about 13.0 MPa, more preferably between about 2.0 MPa and about 3.5 MPa. In two particularly preferred embodiments, the pressure is between about 2.1 MPa and about 2.9 MPa or between about 2.9 MPa and about 3.4 MPa.

15 The process of the invention is particularly applicable to the treatment of industrial and consumer waste.

20 The catalyst is employed to increase the rate of reaction. Suitable catalysts include, but are not limited to, the transition metal ions and mixtures thereof. Preferably, the catalyst is copper (II) ions, iron (II) ions or manganese (II) ions, or a mixture thereof. More preferably, the catalyst is copper (II) ions.

25 Advantageously, oxidation is carried out as a continuous process wherein the feedstock is continuously introduced into the reactor and the vapour phase continuously removed from the reactor.

The oxidation products in the vapour phase removed from the reactor may be recovered by reducing the temperature and pressure of the vapour phase. Accordingly, in another aspect, the present invention provides an oxidation product when produced by a process of the invention.

30 In a preferred embodiment, the oxidation product is acetic acid, formic acid, carbon dioxide or a mixture thereof.

In another aspect, the present invention provides a non-volatile salt when produced by an oxidation process of the invention.

5 Although the present invention is broadly as defined above, those persons skilled in the art will appreciate that the invention is not limited thereto and that the invention also includes embodiments of which the following description gives examples.

## DESCRIPTION OF THE DRAWINGS

10 Figure 1 is a schematic diagram of apparatus particularly suitable for performing an oxidation process of the invention on a laboratory scale.

Figure 2 is a schematic diagram of the additional modifications which may be made to the apparatus of Figure 1 to facilitate the treatment of slurries.

15

Figure 3 is a schematic diagram of a proposed pilot plant or commercial plant design.

Figure 4 is a graph of COD and temperature vs time for the oxidation of glucose at 200°C in a process of the invention.

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Figure 5 is a graph of pH and temperature vs time for oxidation of glucose at 200°C in a process of the invention.

## DETAILED DESCRIPTION OF THE INVENTION

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The present invention is broadly directed to the oxidation of various substances, conveniently described herein as "Phase Transfer Wet Oxidation".

Accordingly, in a first aspect, the present invention provides a process for wet oxidation  
30 of a feedstock comprising at least one non-volatile oxidisable material, which process includes at least the steps of:

- (a) continuously introducing the feedstock into a reactor;
- (b) contacting the feedstock at temperature and pressure with an oxidant in the presence of a catalyst to produce a vapour phase comprising at least some oxidation products and a liquid phase; and
- 5 (c) continuously removing at least some of the vapour phase comprising at least some oxidation products from the reactor while retaining the liquid phase in the reactor.

The term "feedstock" as used herein includes, but is not limited to, aqueous liquids, solutions, suspensions, colloids, emulsions, and other mixtures. The term may also  
10 include slurries formed from substantially dry material to which is added a suitable aqueous liquid.

The amount of oxidisable material in the feedstock is typically less than about 10% by weight.

15

In one embodiment, the feedstock is fed directly into the reactor. In an alternative embodiment, water is firstly introduced into the reactor and then the oxidisable material is introduced into the reactor.

20 The term "contact" as used herein generally means admixing the aqueous solution or slurry with the oxidant in a suitable reactor, which is of a type designed to withstand the temperature and pressure and is well known in the art. Suitable reactors include, but are not limited to autoclaves and pressure reactors.

25 The term "non-volatile" as used herein means that the oxidisable material is largely in the solid or liquid state under the temperature and pressure conditions in the reactor.

It will be appreciated that, preferably, the reactor is one in which the interfacial area between the oxidant and the feedstock is maximised, and from which the reaction  
30 products and the volatile non-oxidisable components present in the feedstock (for example, water) may be readily removed in the vapour phase.

The vapour phase is removed from the reactor while the liquid phase is retained in the reactor.

5 In one embodiment, phase separation may be achieved by keeping the reaction pressure near to the vapour pressure of water at the reaction temperature by, for example, rapidly lowering the pressure of the reactor to remove volumes of treated material by flash vaporisation at specific intervals.

10 The feedstock may be introduced into the reactor by means of a pump or hydraulic plunger or by other means as are known in the art. Optionally, the reactor may incorporate a means of stirring the contents, if and when required.

15 It will be appreciated that the temperature and pressure at which the process of the invention is operated are selected according to the stability or ease of oxidation of the feedstock. The temperature at which the process is operated is generally between about 100°C and 350°C and the pressure between about 0.7 MPa and about 17.2 MPa.

20 Preferably, the temperature at which the process is operated is between about 190°C and about 300°C, more preferably between about 190°C and about 280°C. In two particularly preferred embodiments, the temperature is between about 190°C and about 210°C or between about 220°C and about 240°C.

25 Preferably, the pressure at which the process is operated is between about 1.4 MPa and about 13.0 MPa, more preferably between about 2.0 MPa and about 3.5 MPa. In two particularly preferred embodiments, the pressure is between about 2.1 MPa and about 2.9 MPa or between about 2.9 MPa and about 3.4 MPa.

30 The present invention also contemplates processes in which the feedstock is at the desired temperature and/or pressure prior to entering the reactor, for example a process in which the feedstock comprises a mixture of non-volatile oxidisable material and superheated steam.



While the oxidisable substances are relatively non-volatile, their primary wet oxidation products are generally much more volatile compounds such as carbon dioxide, acetic acid, and formic acid. It will therefore be understood that while the feedstock is introduced to the reactor in the liquid or solid phase, the products of the oxidation reaction may be removed from the reactor in the vapour phase, hence the name "Phase Transfer Wet Oxidation".

Accordingly, a significant portion of the oxidation products from a process of the invention is removed in the gas phase. This is in contrast to the known processes in which the reaction products are generally removed in the liquid phase.

It will be appreciated that any compound which is volatile at the reaction temperature may be present in the gas phase. However, any higher molecular weight compounds, such as higher organic acids, will generally be present at very low concentrations.

The oxidation products in the vapour phase removed from the reactor may be recovered by reducing the temperature and pressure of the vapour phase. Accordingly, in another aspect, the present invention provides an oxidation product when produced by an oxidation process of the invention.

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Typical oxidation products include, but are not limited to, carbon dioxide, formic acid, acetic acid, higher organic acids and mixtures thereof.

In a preferred embodiment, the oxidation product is acetic acid, formic acid, carbon dioxide or a mixture thereof.

More preferably, the oxidation product is acetic acid or a mixture of acetic acid and formic acid. The acetic acid so provided is sterile. Accordingly, the acetic acid may be converted to acetate and utilised as a nutrient source for micro-organisms.

Advantageously, the temperature and pressure of the vapour phase removed from the reactor is reduced in a heat exchanger and the heat recycled to the incoming feedstock. In

another embodiment, the incoming feedstock and the reactor contents are optionally heated by the addition of external heat.

Advantageously, the oxidation process of the invention is carried out as a continuous  
5 process wherein the feedstock is continuously introduced into the reactor and the vapour phase continuously removed.

Because the oxidation is carried out as a continuous process, it will be appreciated that the reactor may advantageously incorporate a means of measuring the liquid level within the  
10 reactor, such that the reactor does not run dry.

If a mixture of oxidisable substances is subjected to a process of the invention, then those with a faster rate of reaction will oxidise first, and the products of the reaction are removed in the vapour phase as they are formed. More stable substances, with a  
15 correspondingly slower rate of reaction, will remain in the reactor until they have oxidised to volatile products. Any water in the feedstock entering the reactor will also be vaporised, thereby permitting more feedstock to enter the reactor. This is in contrast to the known processes, which require either a large reactor, or provide a reduction in the percent conversion of oxidisable substances to their oxidation products.

20

The catalyst is employed to increase the rate of reaction. Suitable catalysts include, but are not limited to, the transition metal ions and mixtures thereof. Preferably, the catalyst is copper (II) ions, iron (II) ions or manganese (II) ions, or a mixture thereof. More preferably, the catalyst is copper (II) ions.

25

While it will be appreciated that the process of the invention is amenable to heterogeneous catalysis, the catalyst may advantageously be in the form of a homogenous catalyst. In the known processes, the use of homogenous catalysts generally leads to catalyst leaching and subsequent contamination of the downstream products. However, it  
30 will be appreciated that, in a process of the present invention, the catalyst may remain in the dissolved liquid phase in the reactor. In this way an initial amount of catalyst may be introduced into the reactor, where it will remain while multiple volumes of feedstock are introduced into the reactor and the oxidation products removed in the vapour phase.

exchanger HX2 which may recycle the heat recovered from the oxidation products removed in the vapour phase by cool-down heat exchanger HX3. It will be appreciated that the feedstock need be heated only to make up the heat balance of the reaction.

5 An oxidant would be introduced into the reactor vessel through inlet GI1. Contact between the oxidant and the liquid phase will then be promoted by means of a stirrer STR2 which mixes the reactor contents. The liquid level within the reactor may be monitored by a system of level sensors LS1 connected to a suitable process control system.

10

The temperature of the liquid phase in the reactor would be controlled by a heating unit and heat exchanger HX4 by means of the recirculating loop RL1 and pump LP4. HX4 may also recycle the heat recovered from the oxidation products removed in the vapour phase by cool-down heat exchanger HX3

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The vapour phase products of the oxidation reaction would be separated from the liquid phase and removed from the reactor through cool-down heat exchanger HX3. The temperature and pressure of the product stream is thereby reduced. The resultant product stream would pass into liquid trap LT2 where gas phase reaction products such as carbon dioxide may be recovered from the mix of uncondensed gases at outlet GO1 while liquid phase reaction products such as water, formic acid and acetic acid may be recovered at outlet LO1.

20

The reactor could be emptied, when required, through outlet LO2 and the heat from the reactor contents may be recovered by heat exchanger HX5. Accordingly, useful non-volatile salts which accumulate in the reactor may be recovered and any catalyst used may be recycled or subject to suitable disposal.

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## INDUSTRIAL APPLICATION

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It will be appreciated that, in use, the present invention provides a process for oxidising a feedstock which may be applied to the treatment of industrial waste. Advantageously, the reactor may be of a significantly smaller volume than that used in known processes due to

the removal of both water and volatile oxidation products from the reactor in the vapour phase, allowing for further feedstock to enter the system. In this way the process may be operated in a continuous manner.

- 5 In addition, a homogenous catalyst may be used in the treatment of more stable compounds, and the catalyst retained in the reactor while multiple volumes of waste are treated. A variety of consumer and industrial waste is amenable to treatment by a process of the invention, and these are discussed above.
- 10 Furthermore, the present invention also provides a sterile source of, for example, acetic acid which may be utilised, following conversion to acetate, as a nutrient source for micro-organisms.

- Those persons skilled in the art will further appreciate that the present description is  
15 provided by way of example only and that the scope of the invention is not limited thereto.

## REFERENCES

- 20 1. Kolackowski, S., Plucinski, P., Beltran, F., Rivas, F., McLurgh, D. "Wet air oxidation: a review of process technologies and aspects in reactor design", *Chem. Eng. J. (Lausanne)*, 1999, 73, 2, 143-160.

## CLAIMS

1. A process for wet oxidation of a feedstock comprising at least one non-volatile oxidisable material, which process includes at least the steps of:
  - 5 (a) continuously introducing the feedstock into a reactor;
  - (b) contacting the feedstock at temperature and pressure with an oxidant in the presence of a catalyst to produce a vapour phase comprising at least some oxidation products and a liquid phase; and
  - 10 (c) continuously removing at least some of the vapour phase comprising at least some oxidation products from the reactor while retaining the liquid phase in the reactor.
- 15 2. A process as claimed in claim 1 wherein the feedstock is an aqueous liquid, solution, suspension, colloid, emulsion or other mixture.
3. A process as claimed in claim 1 or claim 2 wherein the feedstock comprises a slurry formed from substantially dry material to which is added an aqueous liquid.
- 20 4. A process as claimed in any one of claims 1 to 3 wherein the oxidisable material comprises less than about 10% by weight of the feedstock.
5. A process as claimed in any one of claims 1 to 4 wherein the oxidisable material comprises a mixture of substances.
- 25 6. A process as claimed in any one of claims 1 to 5 wherein the oxidisable material is a waste product.
7. A process as claimed in claim 6 wherein the waste product is industrial waste, consumer waste or a component thereof.
- 30 8. A process as claimed in claim 6 or claim 7 wherein the oxidisable material is waste selected from the group consisting of: dairy shed waste; pig and chicken waste; milk processing plant waste; milk, cheese and butter vat wash downs; food

processing waste; waste from the wine industry and brewing industry; food waste; shipboard waste; waste in environmentally sensitive locations; waste from the wash downs and oil-traps of petroleum service stations and garages; waste fats and proteins from the meat processing industry; wool-scouring waste; sewage; medical waste; fibre, ink and polymeric material from the deinking waste produced in the recycling of paper; waste paper and paper products; waste from the wood processing industry including waste wood and wood products, wood fibre, saw dust and wood treated with preservatives; rubber waste; plastic waste; and tannin and colorants from wood pulping streams.

9. A process as claimed in any one of claims 1 to 8 wherein the process is applied to the reclamation of sites contaminated by organic materials.

10. A process as claimed in claim 9 wherein said site is selected from the group consisting of: petrochemical works; gas works; timber treatment sites; and agrochemical sites.

11. A process as claimed in any one of claims 1 to 7 wherein the oxidisable material comprises an organic substance.

12. A process as claimed in claim 11 wherein the organic substance is selected from the group consisting of: lipids; proteins; carbohydrates; mineral oils; vegetable oils; waxes; and hydrocarbons.

13. A process as claimed in claim 12 wherein the organic substance is a carbohydrate selected from starch and cellulose.

14. A process as claimed in any one of claims 1 to 13 wherein the oxidisable material includes one or more oxidisable inorganic compounds.

15. A process as claimed in any one of claims 1 to 14 wherein the oxidant is selected from the group consisting of: air; oxygen; ozone; peroxide; and mixtures thereof.

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16. A process as claimed in claim 15 wherein the oxidant is selected from the group consisting of: air; oxygen; and peroxide.
17. A process as claimed in any one of claims 1 to 16 wherein the temperature is  
5 between about 100°C and about 350°C.
18. A process as claimed in any one of claims 1 to 17 wherein the temperature is between about 190°C and about 300°C.
- 10 19. A process as claimed in any one of claims 1 to 18 wherein the temperature is between about 190°C and about 280°C.
20. A process as claimed in any one of claims 1 to 19 wherein the temperature is between about 190°C and about 210°C.
- 15 21. A process as claimed in any one of claims 1 to 19 wherein the temperature is between about 220°C and about 240°C.
22. A process as claimed in any one of claims 1 to 21 wherein the pressure is between  
20 about 0.7 MPa and about 17.2 MPa.
23. A process as claimed in any one of claims 1 to 22 wherein the pressure is between about 1.4 MPa and about 13.0 MPa.
- 25 24. A process as claimed in any one of claims 1 to 23 wherein the pressure is between about 2.0 MPa and about 3.5 MPa.
25. A process as claimed in any one of claims 1 to 24 wherein the pressure is between about 2.1 MPa and about 2.9 MPa.
- 30 26. A process as claimed in any one of claims 1 to 24 wherein the pressure is between about 2.9 MPa and about 3.4 MPa.

27. A process as claimed in any one of claims 1 to 26 wherein the catalyst is a homogenous catalyst.
28. A process as claimed in any one of claims 1 to 27 wherein the catalyst is selected  
5 from the group consisting of the transition metal ions and mixtures thereof.
29. A process as claimed in any one of claims 1 to 28 wherein the catalyst is selected from the group consisting of: copper (II) ions; iron (II) ions; manganese (II) ions; and mixtures thereof.
- 10 30. A process as claimed in any one of claims 1 to 29 wherein the catalyst is copper (II) ions.
31. A process as claimed in any one of claims 1 to 30 wherein the vapour phase is  
15 removed from the reactor by flash vaporisation.
32. A process as claimed in any one of claims 1 to 31 further including the step of reducing the temperature and pressure of the vapour phase to recover at least one oxidation product.
- 20 33. A process as claimed in claim 32 wherein the oxidation product is selected from the group consisting of: carbon dioxide; formic acid; acetic acid; higher organic acids; and mixtures thereof.
- 25 34. A process as claimed in claim 32 or claim 33 wherein the oxidation product is selected from the group consisting of: acetic acid; formic acid; carbon dioxide and mixtures thereof.
- 30 35. An oxidation product when produced by a process as claimed in any one of claims 32 to 34.
36. A process as claimed in any one of claims 1 to 34 further comprising the step of recovering at least one non-volatile salt from the liquid phase.



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37. A process as claimed in claim 36 wherein the non-volatile salt is recovered as a concentrated solution or a precipitate.
38. A process as claimed in claim 36 or claim 37 wherein the non-volatile salt is an inorganic wood preservative.
39. A non-volatile salt when produced by a process as claimed in any one of claims 36 to 38.